

New Insights on the Structure of Electrochemically Deposited Li Metal and Its Solid Electrolyte Interphase via Cryogenic FIB & TEM

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2018 DOE Vehicle Technologies Office Annual Merit Review

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Overview

Timeline

- Project start date: December 2016
- Project end data: October 2021
- Percent complete: 30%

Budget

- Total project funding 50M
 - DOE share:100%
- FY2017 funding: 10M
- FY2018 funding: 10M

Barriers

- **Abuse Tolerance:** Li-metal based batteries have a long history of problematic dendrite growth
- **Life:** Cells containing Li metal anode still suffer major cycle and calendar life issues.
- **Performance:** Challenging “cold start” requirement at -30 °C.

Partners

- Battery500 and BMR
- PNNL, ARL and INL
- South 8 technology and Maxwell technology

Relevance/Objectives

□ Overall objective

- Explore the nature of Li metal and its SEI
- Improve the cycle life of Li-metal based batteries at room and low temperature

□ Objectives this period

- Quantify the structure of the electrochemically deposited Li metal (EDLi)
- Stabilize Li/electrolyte interface
- Explore novel electrolyte for low temperature use

□ Impact

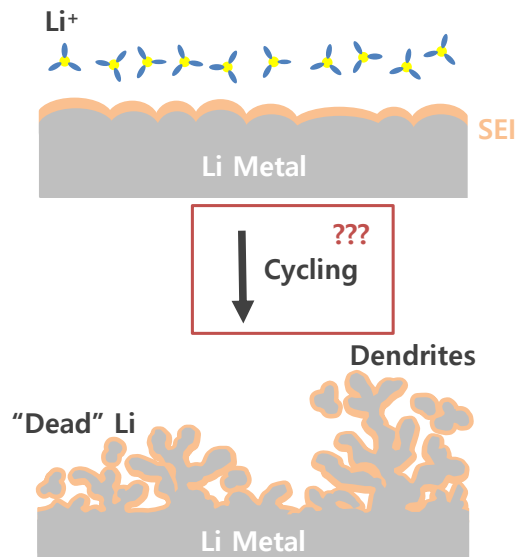
- Bridge the gap between strategies and performance
- Accelerate the practical use of Li-metal based batteries
- Increase durability in low temperature environment

Milestones

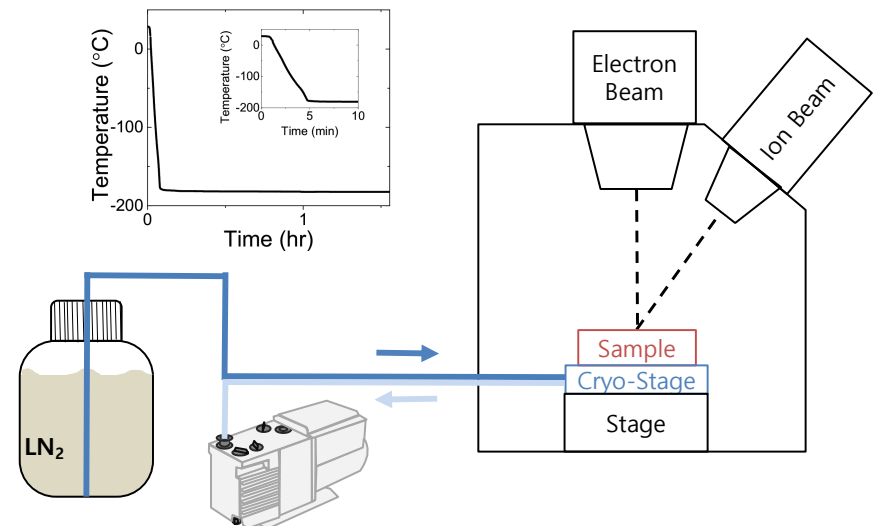
Date	Milestones	Status
December 2017	<u>Milestones:</u> Develop stable electrolytes for room and low temperature use	Complete
March 2018	<u>Milestones:</u> Investigate the influence of the current density on Li metal	Complete
June 2018	<u>Milestones:</u> Establish the proper imaging and diagnosis of Li metal anode with different electrolytes and electrolytes additives	On track
September 2018	<u>Milestones:</u> Develop and implement methods to improve and understand cycles and calendar life of full cells	On track

Approach

- Develop cryogenic electron microscope (Cryo-EM) to image and diagnose the Li metal
- Optimize the electrolyte to stabilize the interface between electrolyte and Li metal
- Quantify SEI components and "Dead" Li with advanced diagnosis methods

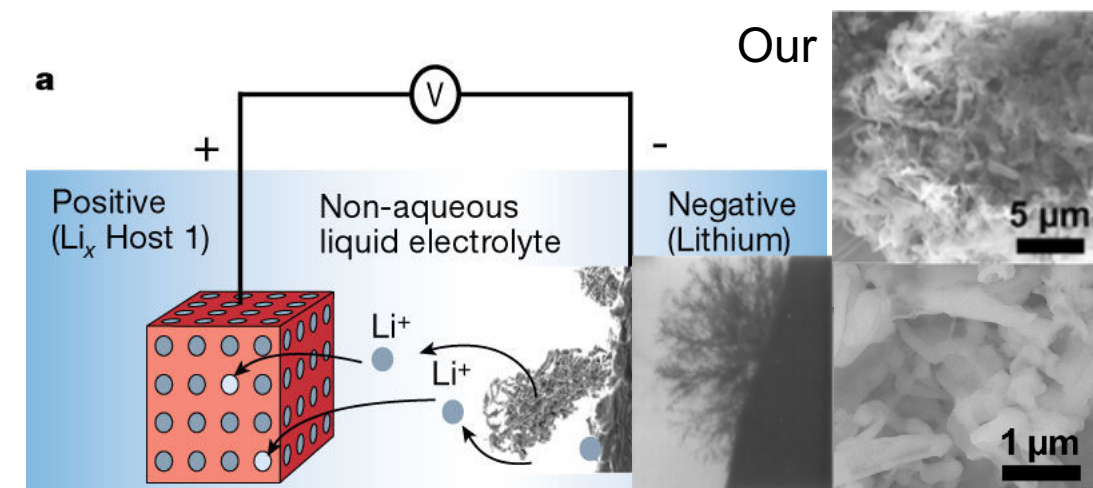


Cryo-FIB



Technical progress

Grand Challenge - Li metal



Tarascon, Nature, 2001

R.R.Chianelli, 1979

Low CE

'Dead' metallic Li

Reacted Li with electrolyte

Ribbon/whisker/dendrite

High surface

Scientific Gaps:

1. What is the true CE ??? Depositing Li, Li₂O, Li₂CO₃, LiOH, LiF

2. Not all Li are the same - Li Foil, Vapor Deposited Li (VDLi) and Electrochemically Deposited Li (EDLi)

3. Substrate/Separator/Electrolyte (Avoid studying things in vacuum)

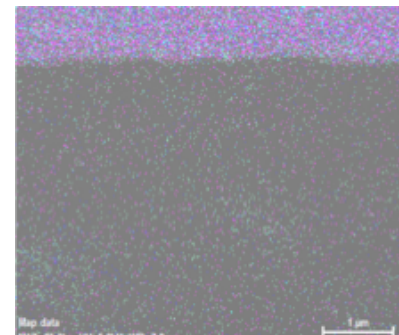
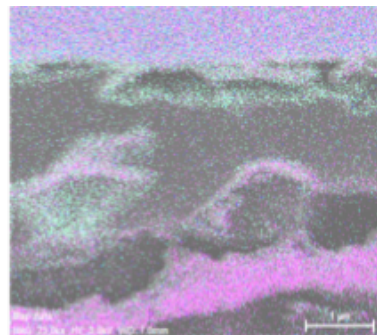
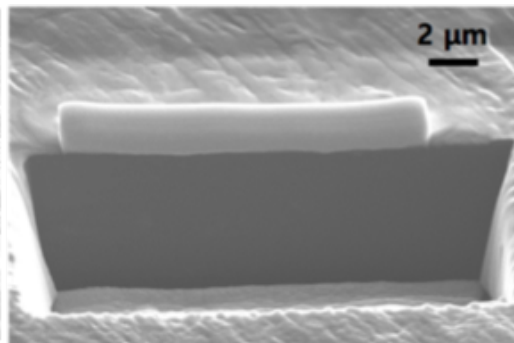
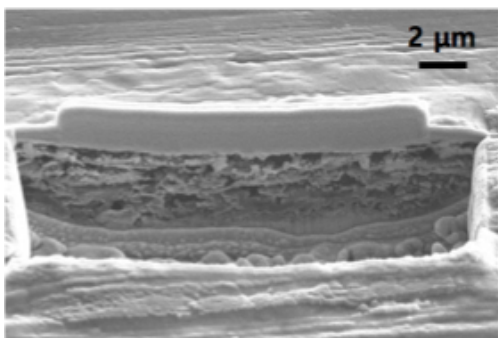
Technical progress

1. Micro structure of Li metal film by Cryo FIB/SEM

- Commercial Li metal

Room Temp (22 °C)

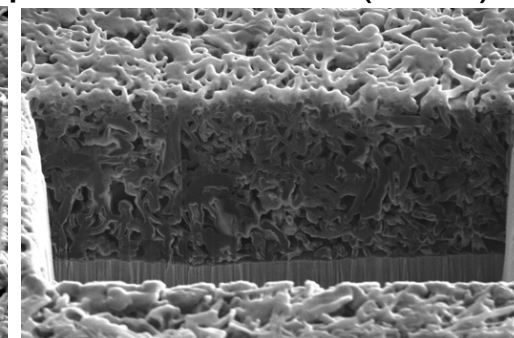
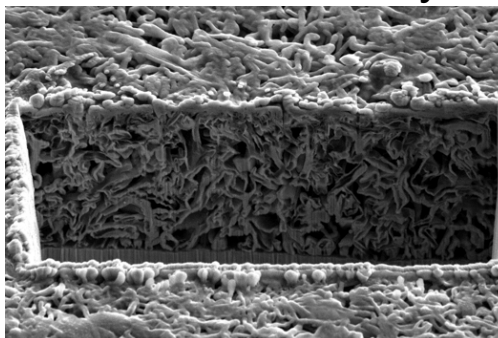
Cryo (-170 ° C)



Pt O C Ga

Severe beam damage and Ga contamination

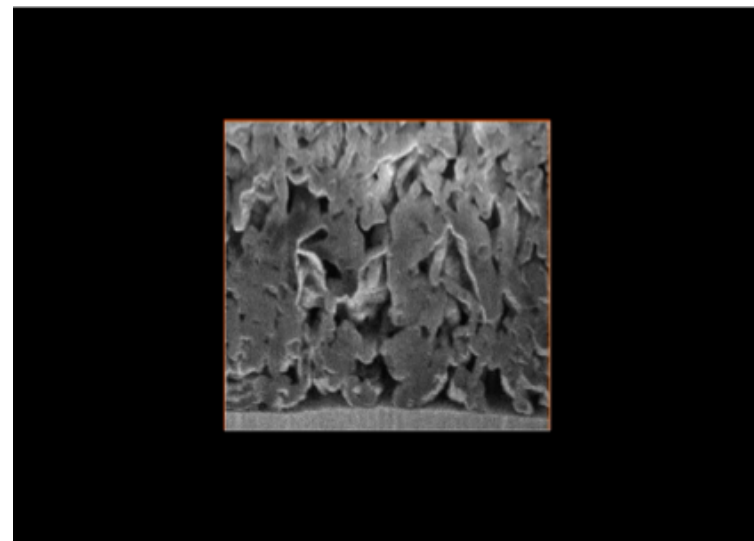
- Electrochemically deposited Li metal (EDLi)



1.2M LiPF₆ (3:7) EC:EMC, 0.5 mA/ cm²

Porous EDLi film

5 μm



Void space

Substrate

Technical progress

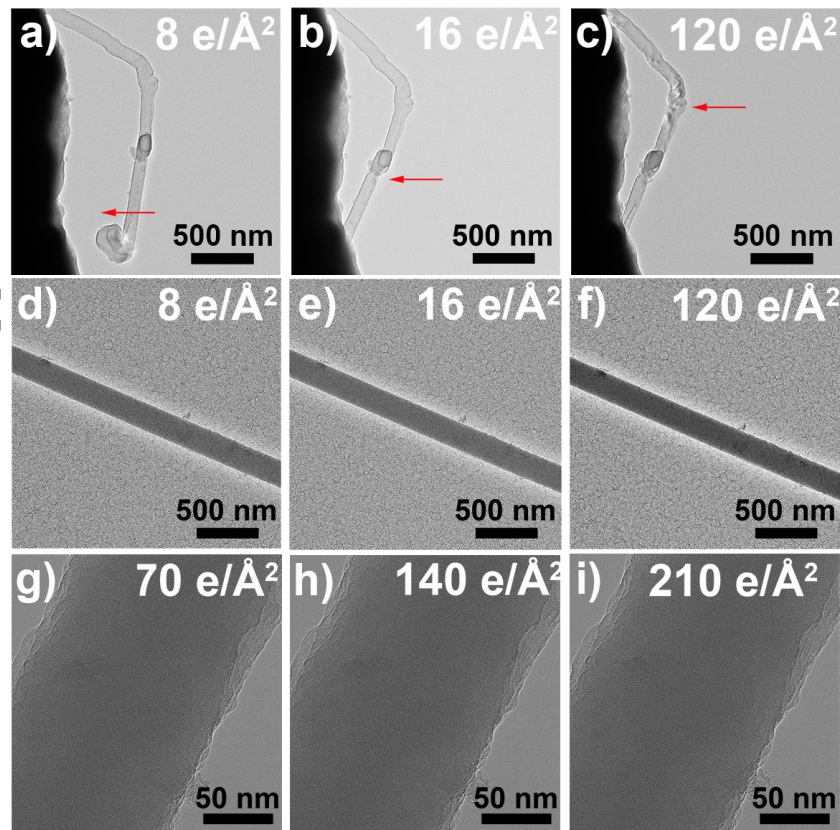
2. The critical need for Cryo TEM



22 °C
Unstable Li metal
Unable to image

-180 °C

Stable Li metal
Atomic resolution
500 kx

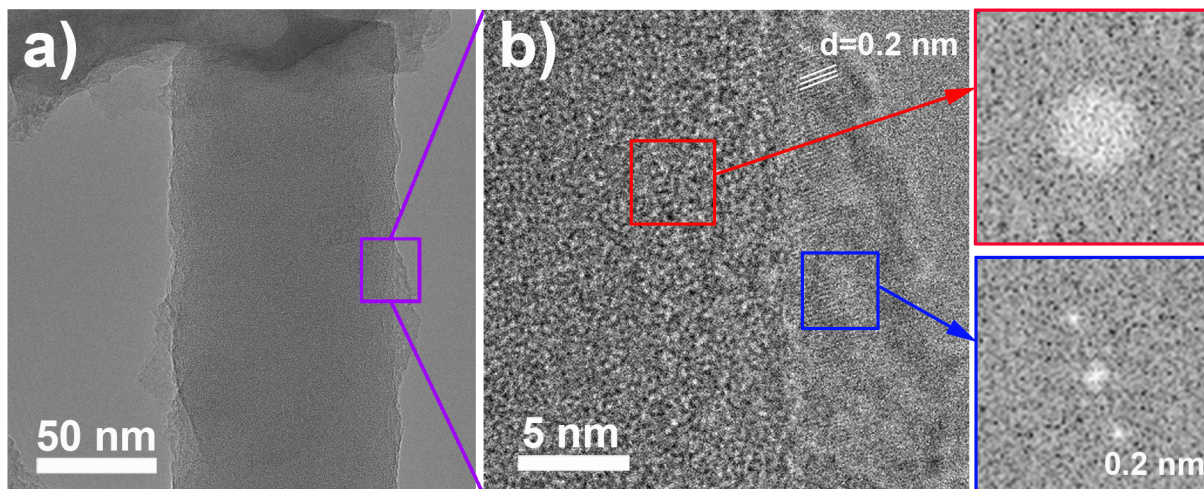


Cryo TEM allows to image the Li metal at a high magnification with low dose.

Technical progress

3. Nanostructure of electrochemically deposited Li EDLi

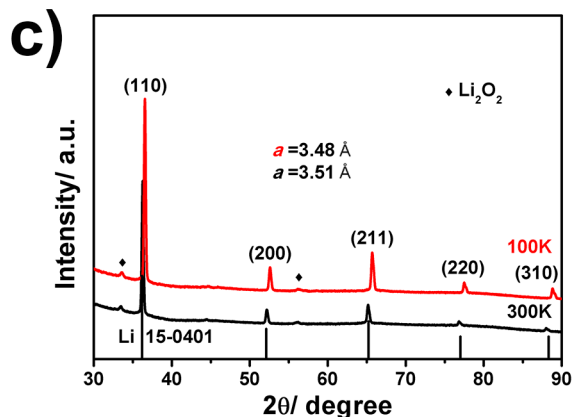
0.5mA/cm² for 5 minutes



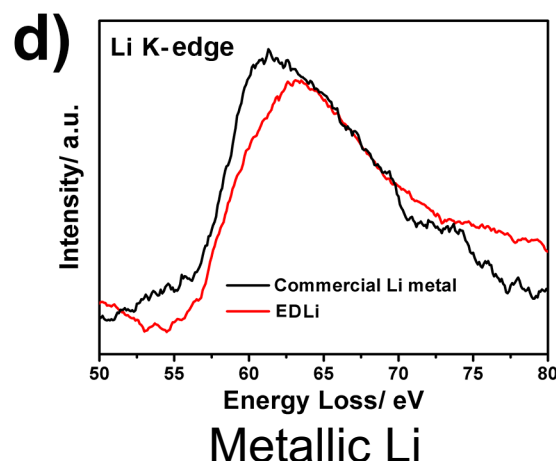
Uneven SEI

Amorphous Li bulk

Crystalline LiF in SEI



No phase transition

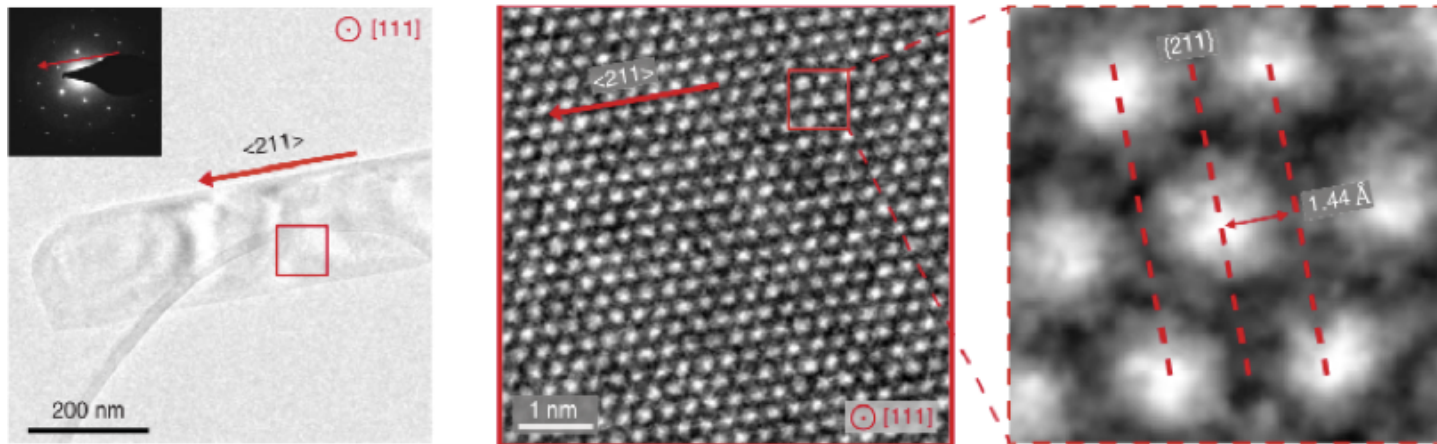


Xuefeng Wang et. al.
Nano Letters 2017

Technical progress

4. Atomic resolution imaging of EDLi

2.5mA/cm² for 30 minutes

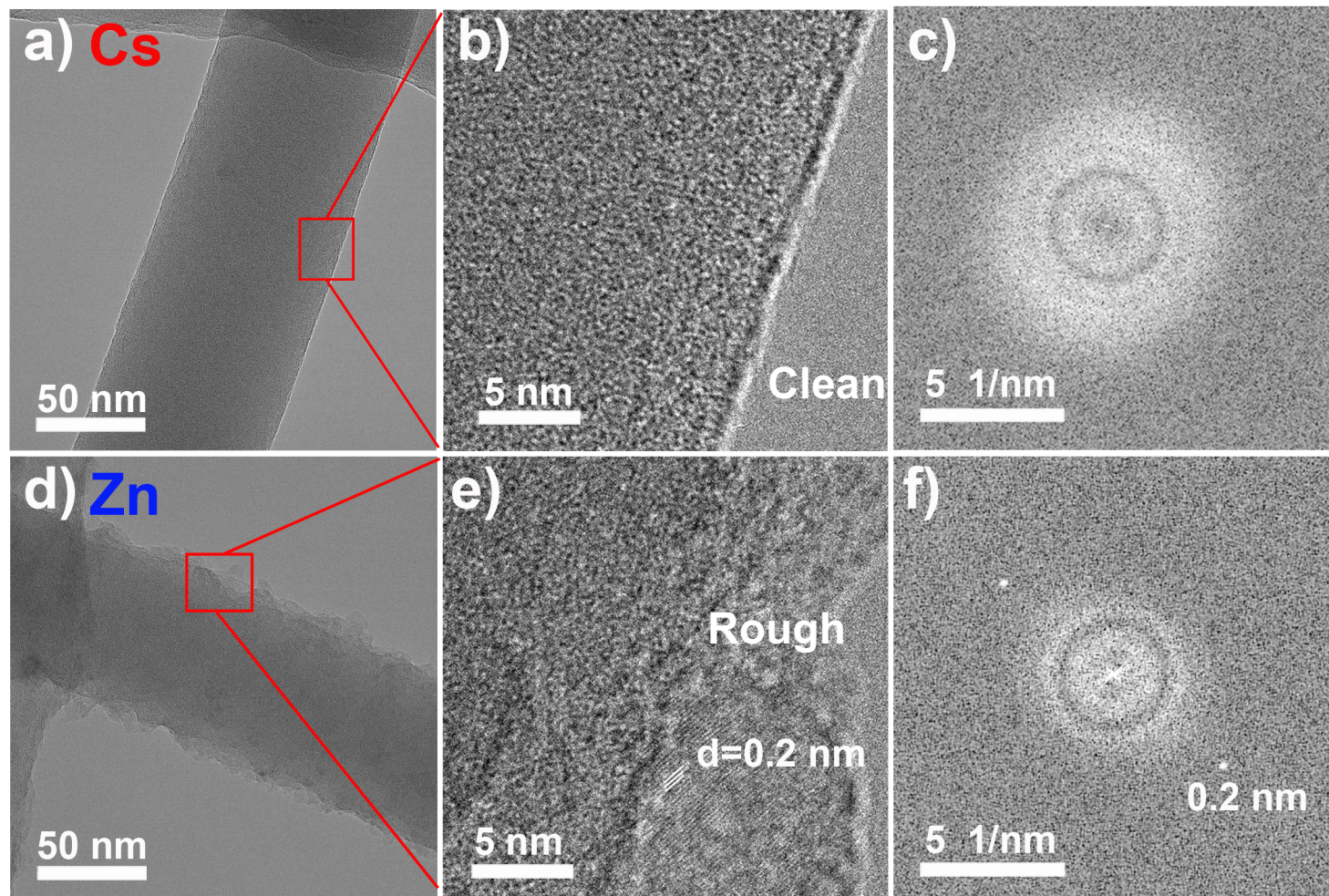


Atomic structure of crystalline Li metal

Yuzhang Li, et. al. Science 2017

Technical progress

5. Additives lead to distinctive SEI



Additives affect SEI property

Clean Surface
Electrostatic
Shield Mechanism

Rough Surface
Zn-Li alloy

Xuefeng Wang
et. al. Nano
Letters 2017

Amorphous Li bulk
Crystalline LiF in SEI

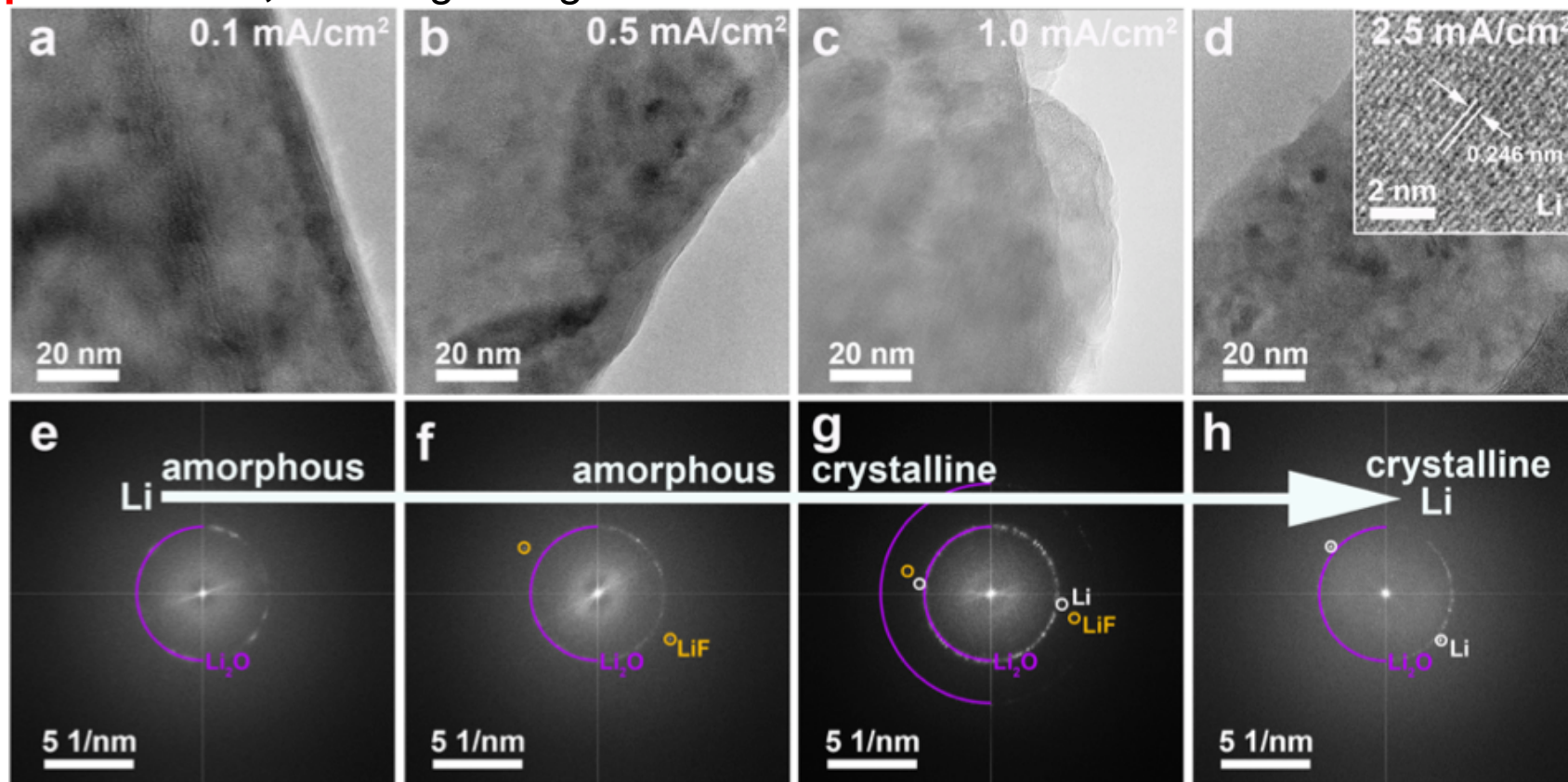
Technical progress

6. Effect of current density on EDLi

Crystalline ED Li, Yuzhang Li, et. al. Science 2017

Amorphous ED Li, Xuefeng Wang et. al. Nano Letters 2017

Vs. 2.5mA/cm² for 30 minutes
0.5mA/cm² for 5 minutes

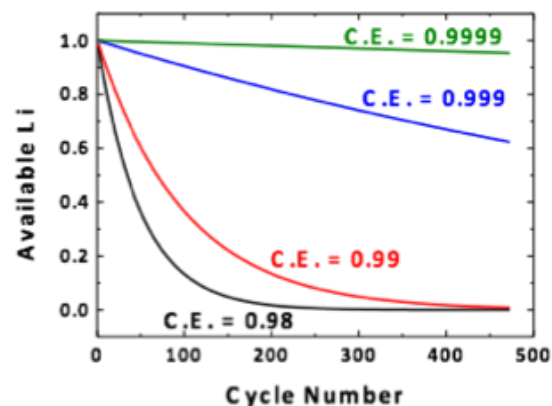


Current density changes the crystallinity of Li metal and SEI properties

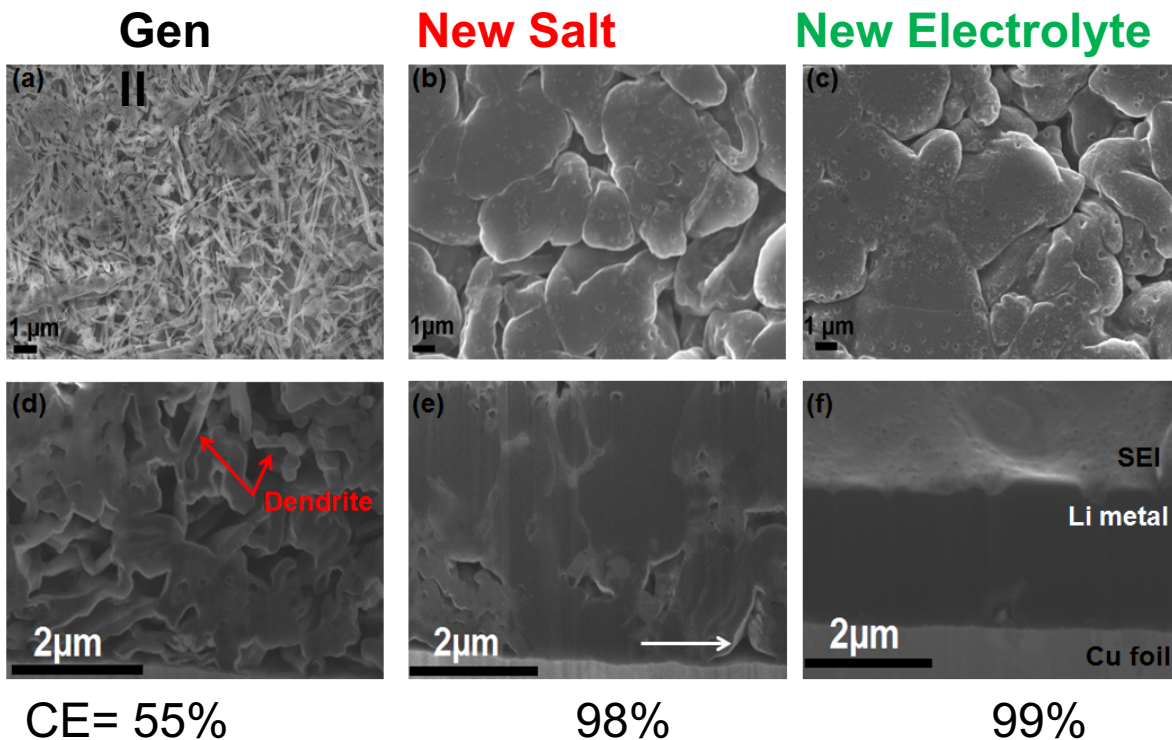
Technical progress

7. Improve EDLi by optimizing electrolyte

Relationship between Coulombic Efficiency (CE) and cycle life



A little lower CE will reduce the cycle number dramatically.



$1\text{mAh/cm}^2 = 5\mu\text{m/cm}^2$, so if you get $6\mu\text{m}$? Porosity in EDLi

Electrolyte with the higher CE results in the denser EDLi film.

Responses to Previous Year Reviewers' Comments

No reviewer comments are available from previous year review on this project.

Partners/Collaborators

➤ **Electrolyte provider and result discuss**

Dr. Jason Zhang, Dr. Wu Xu, Dr. Jie Xiao and Dr. Jun Lu (PNNL)

Dr. Kang Xu and Dr. Marshall Schroder (ARL)

Dr. Boryann Liaw (INL)

➤ **Cryo TEM facility**

Dr. Elizabeth Villa (UCSD/Biological Sciences)

Dr. Xiaoming Pan (UC Irvine)

➤ **Liquefied gas electrolyte**

Dr. Cyrus Rustmoji (South 8 Technology)



Remaining Challenges and Barriers

- ❑ Correlation of a 'good' nanostructure of EDLi and high coulombic efficiency (CE)
- ❑ Determine the 'real' CE and quantify it
- ❑ Quantify the 'dead' Li and divide the percentage between chemically reacted Li and physically isolated Li metal
- ❑ In situ observe the plating and stripping process of Li metal by Cryo-TEM
- ❑ Construct a stable interphase between electrolyte and Li metal

Proposed Future Research

Key Challenges

- a 'good' nanostructure of EDLi
- Quantify the 'dead' Li
- In situ observation by cryo-TEM
- Stable interphase

Future work

- Comparing the nanostructure of EDLi from different conditions (electrolyte, additive, pressure)
- Quantify the dead metallic Li by titration and gas chromatography
- Design the cooling-bias holder
- Protect the Li metal with artificial or in-situ formed film
- Build Li metal based batteries

More team work will be incorporated in the future work

Any proposed future work is subject to change based on funding levels.

Future Team Work

Advancing High Energy Batteries by Design

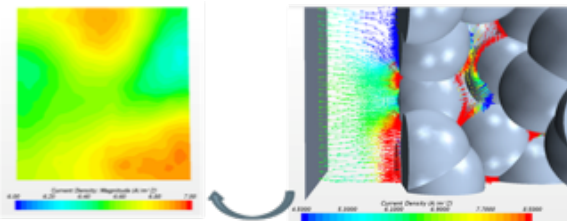
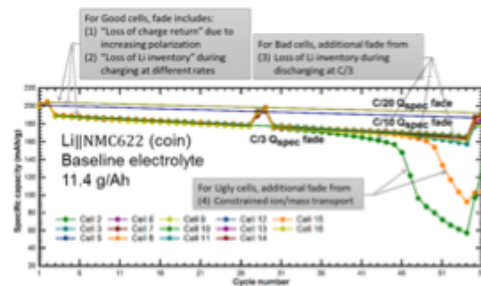


- Fundamental issues related to the use of Li metal electrode directly impact full cell performance
- Failure mode & effect analysis: Advancing battery diagnostics and quantification of performance fade
- Multi-scale HPC simulation and analytics reconcile understanding of interfaces and cell designs

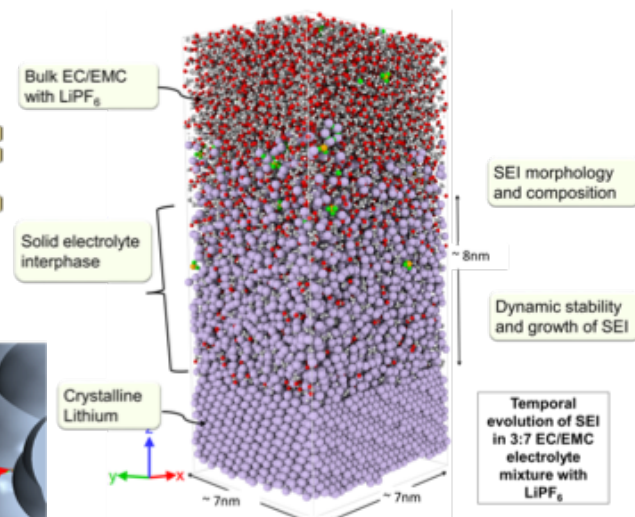
Enhanced understanding of cell design

Identifying Li Failure

Improving performance

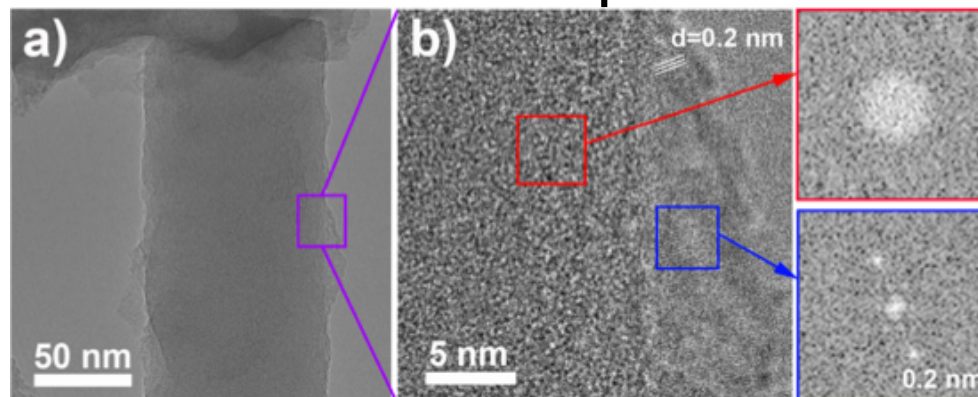


Current Density on Li metal electrode

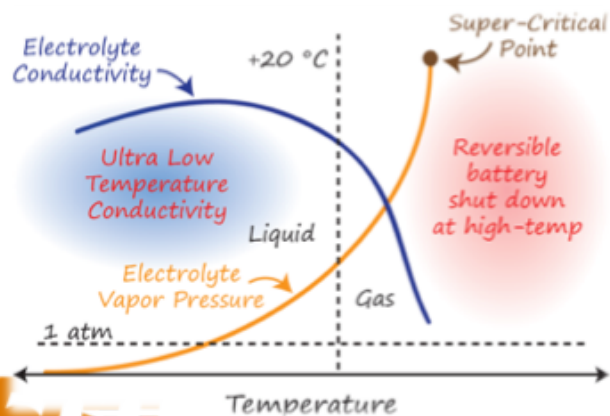


Summary

- ❖ Established cryogenic techniques to explore the nature of Li metal
- ❖ Revealed the nanostructure of EDLi: amorphous Li and crystalline LiF



- ❖ Proposed liquefied gas electrolyte



FM based with 0.2M LiTFSI/LiFSI
25-50MPa

First cycle efficiency >92%
Stabilizing efficiency >99.5%